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Phycobiliproteins form highly efficient light absorbing systems in certain algae. We have investigated the charge-transport phenomena in these individual proteins by analyzing the current-voltage and photocurrent characteristics on Au-phycobili-Au junctions. A photovoltaic effect has been observed in the Au-phycoerythrin-Au junction. At an intensity level of 20 mW, photocurrent closely follows Onsager's law of geminate recombination in 3-dimensions.

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PHOTOVOLTAIC EFFECTS AND CHARGE TRANSPORT STUDIES IN PHYCOBILIPROTEINS

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ABSTRACT

Phycobiliproteins form highly efficient light absorbing systems in certain algae. We have investigated the charge-transport phenomena in these proteins by analyzing the dark current-voltage and photocurrent characteristics obtained across Au-phycobiliprotein-Au samples. A photovoltaic effect was observed for Au-phycoerythrin-Au sample. At low intensity levels, the photocurrent closely follows Onsager's law of geminate recombination in three dimensions.

INTRODUCTION

Phycobiliproteins, porphyrins and carotenoids *in supramolecular* assemblies play a central role in energy and electron transfer processes in natural systems. Stacked porphyrin systems have been proposed as potentially useful materials in the fabrication of photovoltaic devices of exceptionally high performance and efficiency [1-2].

Photodynamic proteins containing small pigment chromophores form the photosynthetic apparatus in plants and algae. Photosynthetic pigments comprise a broad category such as chlorophyll, bilins and carotenoids. The role of chlorophylls and bilins have been well-established in the light-harvesting process [3].

In algae, phycobiliproteins form large, highly organized supramolecular antenna complexes called phycobilisomes. These complexes are responsible for harvesting visible light [4-5]. Studies on these complexes have been on isolation and separation of the individual pigment proteins from their native environments [6], crystallographic structure determination [7], and the absorption and fluorescence properties [8-9] of these molecules and assemblies. The molecular structures of some of the phycobilins are shown in Figure 1. Phycoerythrin (PE), phycocyanin (PC) and allophycocyanin (APC) are the individual biliproteins that self-assemble to form the phycobilisomes. The most remarkable feature of this supramolecular complex lies in the ordered hierarchy of the assembly. The absorption and fluorescence properties of each of these individual biliproteins form the basis for this hierarchy. These assemblies are responsible for maximizing the efficiency of light-harvest and energy transfer between the individual biliproteins down to photosystem II [3-5].

In an earlier study, it was demonstrated that phycoerythrin can be incorporated into conducting polymers creating ordered systems possessing unusual optical and electronic properties [10]. In the present investigation,

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we have carried out experiments on pure proteins in order to understand the charge-generation and charge-transport phenomena. These results have been used in delineating the electron transport mechanisms in this important class of proteins.

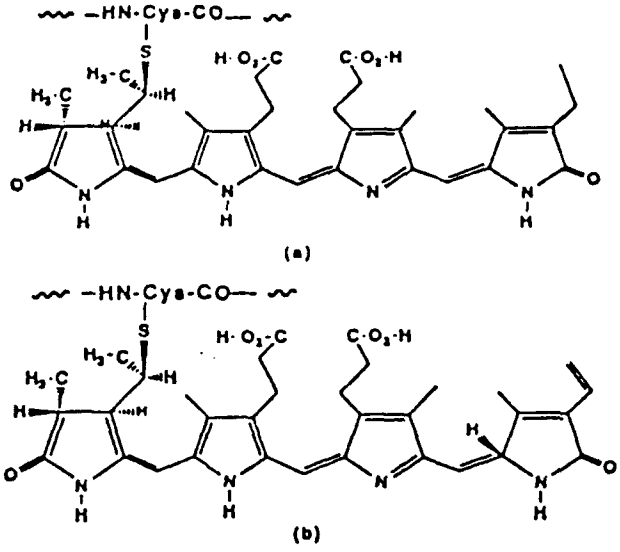

Figure 1 Molecular structure of common phycobilins (a) phycocyanobilin and (b) phycoerythrobilin.

EXPERIMENTAL

Interdigitated gold electrode geometry was used for photoconductivity measurements. These electrodes consisted of digits separated by 15 μm, and of 5000 Å length and 1000 Å thickness. A drop of aqueous protein solution was placed on the electrode. After evaporation of the solvent, thin insulating protein films sandwiched between the Au digits were obtained. The resistance of these films was of the order of several megaohms.

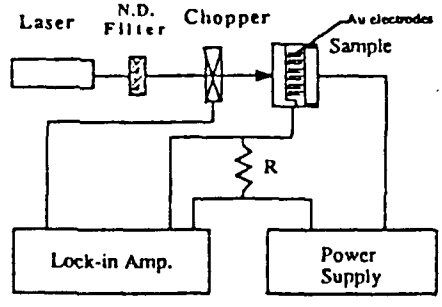

Figure 2 Experimental setup for steady state photoconductivity measurements.

The experimental setup for steady state photoconductivity measurements is shown in Figure 2. Continuous wave (CW) light of wavelength 488nm from an Ar^+ laser was used as the light source. The light beam was chopped at 15 Hz. The signal across a 1 megaOhm resistor, which is in series with the sample, was detected by a lock-in detector. The sample was mounted on a cold finger type cryostat which can be cooled down to 20 K. All the measurements were done in a vacuum better than 10^{-3} torr. The

absorption spectra of the proteins in the thin film form were obtained in the UV-visible range. The dark current-voltage characteristics of the resulting metal-protein-metal configurations were measured in air.

RESULTS AND DISCUSSION

The UV-visible absorption spectra of the proteins PC and PE in thin film form are shown in Figures 3(a) and (b). Both the absorbance and fluorescence spectra of these proteins in their dried thin film form closely resemble their solution spectra (fluorescence spectra not shown here).

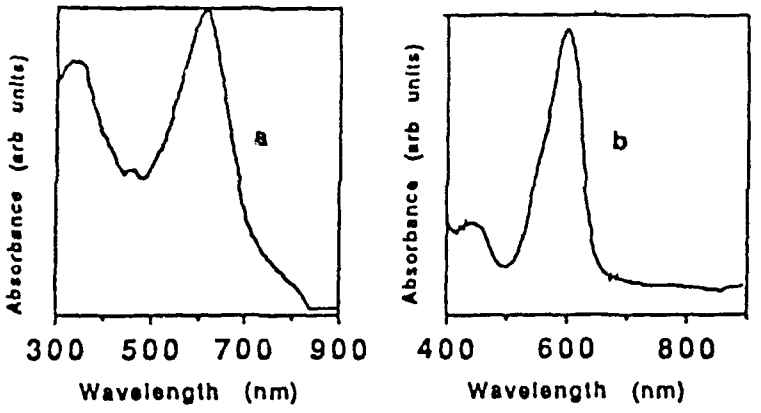

Figure 3 Absorption spectra of (a) phycocyanin and (b) phycoerythrin. thin films.

The dark current-voltage (I-V) characteristics of the Au-protein-Au samples were determined prior to optical measurements. Figures 4(a) and (b) show the I-V characteristics of the proteins PE and PC respectively, as measured in air. From the geometry of the sample, the field across the protein is estimated to be in the range of 10^5 - 10^6 V/m. The non-linear or non-Ohmic nature of the I-V characteristics is apparent from the figure. Such non-linear characteristics could arise either from the bulk material or from the metal/insulator junctions. In the latter case this would suggest to the formation of a barrier across the junction or a possible formation of space-charges near the electrodes. A detailed analysis of the work functions of the proteins and the metal forming the electrode is essential for further elucidation of these characteristics.

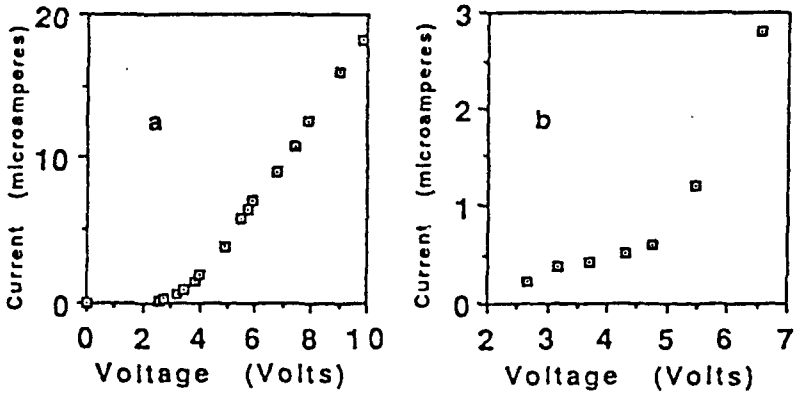

Figure 4 The current-voltage characteristics of (a) Au-PE-Au and (b) Au-PC-Au in air.

Phycoerythrin was chosen for further detailed investigation in the present work. The Au-PE-Au sample was placed in a vacuum chamber. The photocurrent across the sample was measured before and after evacuation. It was observed that photocurrent signals were stronger before evacuation. Steady-state photoconductivity across the Au-PE-Au sample was measured as a function of applied electric field, light intensity and temperature after evacuation. The variation of steady-state photocurrent with intensity at room temperature is shown in Figure 5. The applied voltage across the sample was 70 Volts. It was found that at very low excitation intensities (<1 mW/cm^2) there was negligible photocurrent across the sample. However, at intensities above 1 mW/cm^2, the photocurrent across the sample increases linearly with intensity up to 30mW/cm^2. Saturation of photocurrent is observed at higher intensities.

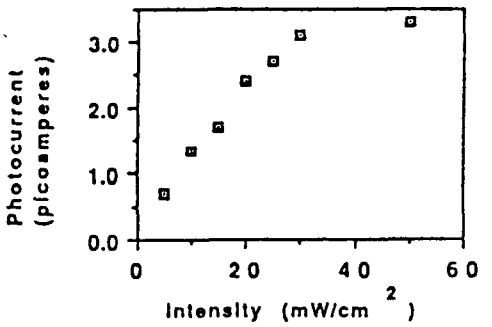

Figure 5 Steady state photocurrent characteristics as a function of intensity at 296 K.

The variation of the photocurrent with the square root of the applied voltage is shown in figure 6 on a semi-log scale. The lower curve corresponds to an excitation intensity of 20 mW/cm^2 and the upper curve to 50 mW/cm^2. The linearity of these characteristics at lower intensity suggests that the photocurrent I follows the relationship

$$I \alpha \exp ((\beta E^{1/2} / kT) - (E_0 / kT))$$

where E is the field across the sample, k is the Boltzmann's constant and T is the absolute temperature. The linearity also indicates that the photocurrent generation closely follows Onsager's law of geminate recombination in three dimensions [11]. At higher intensity, a deviation from this law is observed indicating that other conduction mechanisms dominate in this regime.

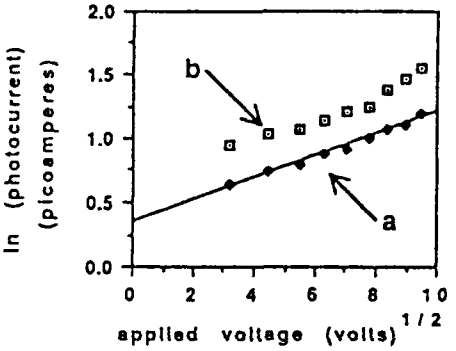

Figure 6 Variation of steady state photocurrent with square root of applied voltage for PE at 296 K (a) 20 mW/cm^2 and (b) 50 mW/cm^2.

The temperature dependence of the photocurrent across the sample was studied at 50 mW/cm^2 light intensity and at an applied voltage of 50 V. Figure 7 shows the functional form of temperature dependence of photocurrent for PE. The photocurrent remains constant at lower temperatures (70 K - 150 K) and increases exponentially at higher temperatures. The activation energy for the process is estimated to be 300 meV.

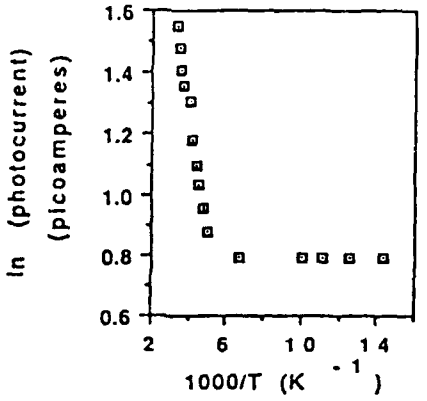

Figure 7 Temperature dependence of photocurrent for PE.

CONCLUSIONS

Au-phycobiliprotein-Au systems were fabricated and their dark I-V characteristics as well as photocurrent characteristics have been investigated. We observed for PE a photovoltage of 0.2 microvolts, 1.9 microvolts and 2.6 microvolts for incident light intensities of 1 mW/cm^2, 20 mW/cm^2 and 50 mW/cm^2 respectively. Non-linear dark I-V characteristics were obtained for both PC and PE. The linear variation of the logarithm of photocurrent with square root of the applied voltage at lower intensities suggests that the photocurrent closely follows Onsager's law of geminate recombination in three dimensions [11]. It is also observed that the photocurrent decreases exponentially with decrease in temperature according to the predictions of Onsager's law. The activation energy obtained from the Arrhenius plot (Figure 7) is estimated to be 300 meV (114.8 x 10^{-17} K. cal).

It should be noted that PE shows photoconducting properties in addition to being a good luminescent material. PE and other phycobiliproteins are strongly fluorescent. Fluorescence implies thermal freeing of trapped carriers which in turn indicates that free charge carriers are formed by the excitation process. The weak dependence of the observed photocurrent magnitude on applied electric field could be attributed to the luminescent properties of PE. Good luminescent materials require rapid recombination while good photoconductors require slow recombination. Simultaneous measurements of luminescence and photoconductivity would give us a deeper knowledge of charge generation, transport and recombination processes [12]. Such investigations will lead to a better understanding of the potential of these proteins in device applications and may lead to a more fundamental appreciation of the biochemistry and photophysics of how they function in the phycobilisome in vivo.

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